

Dielectric behaviour during solidification of *n*-hexadecanol and its mixture with *n*-octanol in non-polar solvents

K N Abdel-Nour, I K Hakim and M A M Eid

Microwave-Physics Department, National Research Centre, Dokki, Cairo, Egypt

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Abstract : The temperature dependence of dielectric constant ϵ' , dielectric loss ϵ'' and d.c. conductivity σ were investigated for *n*-hexadecanol, its mixture with *n*-octanol (1 : 1) and also when mixed with two non-polar solvents of different freezing points (decalin or cyclohexane). For all the investigated solutions except *n*-hexadecanol and its very high concentrations in both solvents, a sharp drop in ϵ' , ϵ'' and σ at the freezing point are obtained. The sharpness of this drop decreases at lower temperatures and eventually reaches a stable value on solidification. For *n*-hexadecanol and its very high concentrations in both solvents, two freezing points were obtained. At the first freezing point during the solidification process, a sudden and large increase in ϵ' , ϵ'' as well as in σ is noticed. These parameters remain high by further cooling till the second freezing point is reached. This region is called the gel phase (α -phase). Beyond the second freezing point, ϵ' , ϵ'' and σ drop rapidly till they reach the stable value on solidification (γ -phase). The region between α and γ phases is called the β -phase. The high values of ϵ' , ϵ'' as well as σ are due to molecular rotations resulting in proton transfer through a sheet of hydrogen-bonded hydroxyl groups. Also, the sharp decrease in the values of ϵ' , ϵ'' and σ corresponds to the change from rotating α -phase to the non-rotating γ -phase.

Keywords : Dielectric properties, d. c. conductivity, temperature dependence

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1. Introduction

Series of measurements were carried out to investigate by the dielectric constant method of the possible rotation of certain molecules in the solid form. Some substances, in particular, the tetra-substituted methane studied by Smyth and his coworkers [1] show a slight rise in dielectric constant on freezing. The interpretation of this is that dipole rotation can still occur in the solid state, so that the increase in density on freezing leads to an increase in the dielectric constant. On the other hand, most polar substances on freezing, show a sharp drop

in dielectric constant to approximately the high-frequency value ϵ_{∞} , showing that in the solid state the permanent dipoles no longer contribute to the polarization. In some cases, it was found that the dielectric constant ϵ' during the solidification, consists in a sudden and a very large increase in ϵ' at the freezing point. By further cooling down the substances, ϵ' remains high until the temperature at which ϵ' drops rapidly to values lower than the dielectric constant of the liquid (the temperature of the second freezing point). The dielectric properties of normal alcohols in the waxy form (*i.e.* α -form) satisfy this result [2–10]. The discussion of this behaviour from the stand point of 'molecular rotation' was done by Smyth and Hoffman [2]. The structure analysis of the normal alcohols showed that three types α , β and γ of the crystal structure have been detected [11]. The first phase which crystallizes initially from the melt on freezing is the α -phase. It is an 'opaque state' and takes the hexagonal structure and is molecular rotating phase. On further cooling, this phase transforms into β -phase at a 'transition point'. In this latter phase, the molecular rotation ceases to occur and the crystal structure changes to ortho-rhombic. Finally, the substance reaches the γ -phase which is the most stable phase. The crystal structure is mono clinic and the molecular rotation does not occur in this phase. For long chain alcohols with odd members of carbon atoms more than 31, another tilted form, δ -phase [7] was detected.

In addition to that, in some substances such as camphor and its derivatives [12,13], or in solution of the palmitic acid in hexane [14,15] for any temperature above and below the freezing point, there is a monotonic increase in the dielectric constant. This proves that reorientation of dipoles can occur in the liquid phase as well as in the solid one (that concerns mainly the spherical or cylindrical shaped molecules).

The measurements of electrical conductivity σ carried out for normal chain alcohols have shown [9] the existence of a similar behaviour, just like the one which occurs in the dependence of ϵ' against temperature.

It is the aim of the present investigation to carry out a systematic study on the dielectric behaviour of n-hexadecanol and n-hexadecanol mixed with n-octanol (1: 1) in the non-polar solvents decalin or cyclohexane. The study extended to include the mentioned substances in the liquid and solid forms aiming at further information about their molecular rotations through a wide range of temperature from 5 to 60°C.

2. Experimental work

The dielectric constant ϵ' and dielectric loss ϵ'' were measured at 50 kHz, using NF-dekometer (WTW, type DK05) of the Schering-bridge type with sample holding cell of the type NFL1. The accuracy is of the order of $\pm 2\%$.

The simple circuit used to measure d.c. conductivity, consists of a power supply unit OM 4516/01 from Philips is used. Its output is a stable d.c. voltage between 0 and 250 volts with a maximum permissible loading current of 1 mA. The potential difference V across the sample holding cell (type NFL1) and the current I flowing through it are measured by a

multimeter type URI-BN1050 from Rhode and Schwarz. The electrical conductivity σ is calculated using the equation [10],

$$\sigma = \frac{I}{3.6 \pi C V} \Omega^{-1} \text{ cm}^{-1}, \quad (1)$$

where C is the effective capacity of the empty cell in pF.

The materials used in this work are pure *n*-hexadecanol (cetyl alcohol), and pure *n*-octanol. Two non-polar solvents as well are used for dilution, namely pure decalin and pure cyclohexane.

Pure *n*-hexadecanol from Fluka AG, Chemische Fabrik CH-9470 Buchs was used after being dried in a desiccator over phosphorous pentoxide for about two weeks. Pure *n*-octanol (97%) was obtained from B.D.H. Chemicals Ltd, Poole, England, it was carefully dried and fractionally distilled several times before use.

Pure decalin (99%) and cyclohexane (99%) were obtained from B.D.H. and used as received.

3. Result and discussion

In the present work, an attempt is made to study the dielectric behaviour and electrical conductivity during solidification of *n*-hexadecanol and its mixture with *n*-octanol (1 : 1) in two non-polar solvents having different melting points (decalin -43°C and cyclohexane $+6.4^\circ\text{C}$) [17]. The dielectric constant ϵ' and dielectric loss ϵ'' were experimentally measured at 50 kHz.

To study the d.c. conductivity σ of the mentioned alcohols, the current I was measured as a function of the applied voltage between 0 and 200 V. The relation between V and I is a straight line from which σ was calculated according to eq. (1). As an example the I - V relation of *n*-hexadecanol is represented in Figure 1.

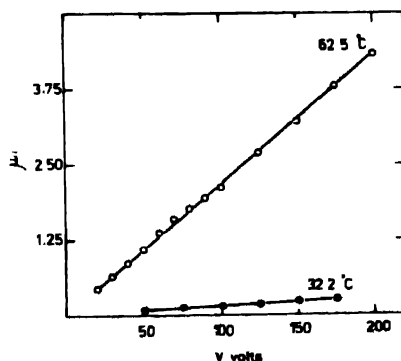


Figure 1. Current-Voltage characteristics for pure *n*-hexadecanol at two different temperatures.

n-Hexadecanol :

For pure *n*-hexadecanol ϵ' , ϵ'' and σ are illustrated graphically in Figure 2 versus the temperature t °C. The values of ϵ' and ϵ'' obtained here are comparable with those reported before [4,9,10,18]. It is clear from this figure that the cooling run and the heating run have different paths.

On cooling, ϵ' , ϵ'' and σ first change slightly with temperature, then rise sharply, flattened, attain some maximum values and finally they drop to slowly varying values. The region of maximum values extends mainly between 49.2 and 43°C as shown in Figure 2. These temperatures are comparable with the transition points found in literature [8], 48.3 and 45.1°C respectively. Cooling rate experiments [18] indicate that these are freezing points.

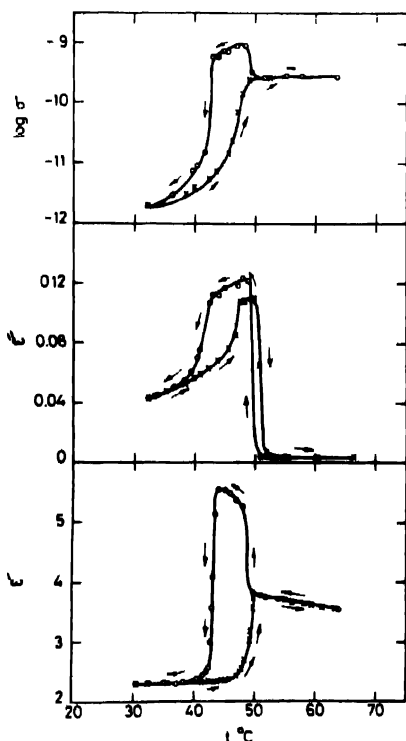
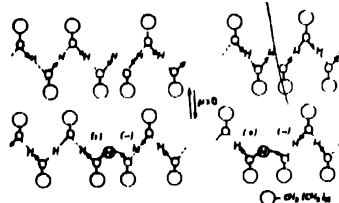
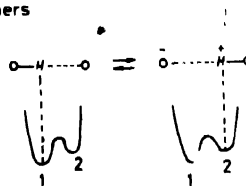


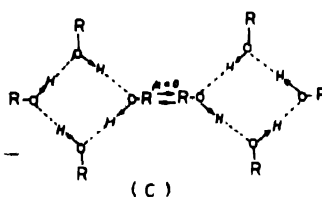
Figure 2. Temperature dependence of the dielectric constant ϵ' , dielectric loss ϵ'' and d.c. conductivity σ for pure *n*-hexadecanol : \circ -cooling, \times -heating.



(a)
Polarization reversal effect of O-H bond in multimers



(b)
The process of proton migration in the bridge O-H...O



(c)
The process of polarization reversal of cyclic tetramers presumably formed in the solid phase

Earlier investigations [18,19] showed that similar hysteresis effects were obtained for gelling solutions, justifying the name 'gel' or ' α ' giving here to the phase between the two freezing points and this was confirmed through X-ray measurements [18,19]. However, in the field of dielectric measurements, this phase is called the rotating phase due to the appearance of the strong anomalous dispersion between the two freezing points. At

Figure 3. The molecular phenomena responsible for the formation of the solid as well as the gel phase during solidification.

temperatures below the second freezing point, a sharp decrease in the value of the dielectric constant is noticed. This phase is called the non-rotating or solid phase (β -phase) [18], which is followed by slowly varying values identifying a stable solid phase (γ -phase) [18].

On heating, ϵ' , ϵ'' and σ rise sharply on approaching the second freezing point. Between the two freezing points ϵ'' changes very slowly and near the first freezing point it drops sharply and finally at higher temperatures coincides with values taken on cooling. However, ϵ' and σ after their sharp rise, coincide with the corresponding values taken on cooling. Thus cooling and heating runs form the shape of a hysteresis loop for ϵ' , ϵ'' and σ .

This result is supported by the infrared (IR) studies [20] indicating differences in the structure of these forms which are consistent with the different phase modifications determined by the X-ray studies [21,22]. These studies indicate that *n*-hexadecanol exhibits α , β and γ phases. The presence of such phases implies certain molecular rearrangements. The formation of multimers through the hydrogen bond chain plays a major role in these rearrangements in the gel as well as the solid phases.

In the liquid phase, the orientational polarization of multimers is disturbed by thermal motion. At the liquid-gel transition region, they pass from a random space distribution of molecules to a slightly ordered one, with greater ease of reorientation.

The polarization reversal effect of the OH-bonds in multimers as shown in Figure 3a is responsible for the high values of ϵ' as well as of ϵ'' and σ in the gel phase. This effect is considered here as a process of reorientation of multimers, which should be understood not as free rotation of systems of molecules but as a phenomenon of rotation simulated by the inversion of the electric moments [23]. It is caused by the transition of protons along the whole chain [24] of bonds from the potential well 1 with lower energy to well 2 with higher energy. Positions 1 and 2 correspond to the two extreme positions of the hydrogen atom in the bridge O-H...O as shown in Figure 3b.

The sudden drop in ϵ' , ϵ'' and σ noticed at the second freezing point is due to a structural change of the chain of hydrogen bonds from the opened to the closed form during transition of the polar gel phase into the non-polar solid phase. Another closed form could be expected. This is the cyclic tetramers form shown in Figure 3c. This form is also subjected to polarization reversal effect as the arrows indicate in Figure 3c.

n-Hexadecanol and *n*-octanol mixture (1 : 1) :

The foregoing study on pure *n*-hexadecanol and pure *n*-octanol makes it valuable to study the dielectric behaviour (ϵ' , ϵ'') and d.c. conductivity (σ) of a mixture containing *n*-hexadecanol and *n*-octanol in the ratio (1 : 1). This study was extended from the liquid to the solid phase with emphasis on changes taking place during solidification. The values of ϵ'' are very small to be measured. However Figure 4 shows the variation, of both ϵ' and σ with temperature.

In the liquid state, it is evident from Figure 4 that ϵ' increase linearly by decreasing temperature while σ attains almost a constant value. On solidification, at the freezing point ($\approx 38^\circ\text{C}$), ϵ' and σ suffer sharp drops followed by a monotonic decrease with further

cooling. This may be due to a sudden restriction in the rotational motion of the dipoles causing no longer contribution to polarization.

During heating, ϵ' and $\log \sigma$ start to rise till a temperature few degrees below the melting point. Further increase in temperature, causes a decrease in ϵ' and σ but at a slower rate. A hysteresis loop is obtained between the cooling and heating runs in the case of ϵ' . In

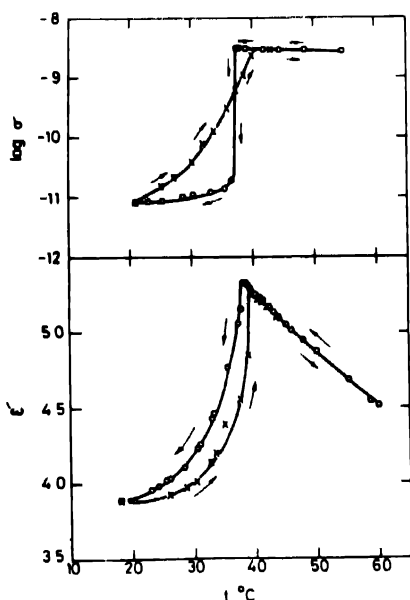


Figure 4. Temperature dependence of dielectric constant ϵ' and d.c. conductivity σ for the mixture of n-hexadecanol with n-octanol (1:1): \circ -cooling, \times -heating

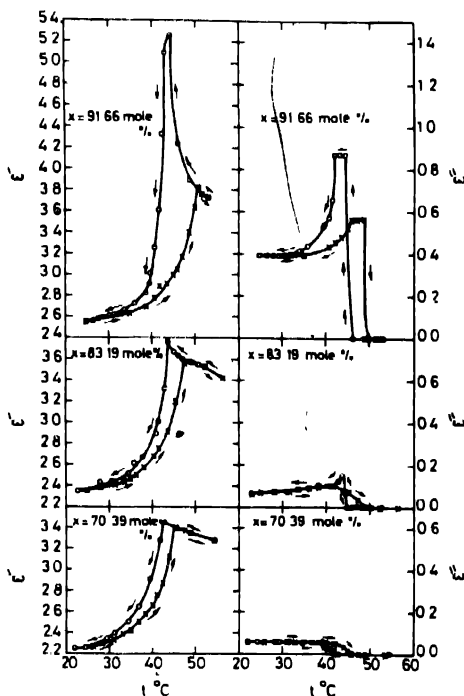


Figure 5. Temperature dependence of the dielectric loss ϵ'' for n-hexadecanol in cyclohexane at very high concentrations: \circ -cooling, \times -heating

the case of d.c. conductivity a different trend is noticed. This could be attributed to the presence of n-octanol in the mixture which is characterized by lower melting point (-17.9°C) [17] and higher d.c. conductivity ($\sigma = 6.5 \times 10^{-8} \Omega^{-1} \text{cm}^{-1}$) compared with those of n-hexadecanol (melting point $= 49^\circ\text{C}$ and $\sigma = 3 \times 10^{-10} \Omega^{-1} \text{cm}^{-1}$). It is to be noticed that no gel phase appears either on cooling or on heating in the investigated mixture. This result agrees with those reported before [25,26-30].

The dielectric behaviour of this investigated mixture on solidification is comparable with that of pure n-dodecanol [2] which crystallizes directly into a stable form and it gives no evidence to molecular rotation, *i.e.* there is no gel phase appearing during solidification. This could be inferred to the similarity of their concentration of dipoles N ($N = 26.5 \times 10^{20} \text{cm}^{-3}$) in the temperature range from the liquid phase to the solid phase. 10^{20}

n*-Hexadecanol and its mixture with *n*-octanol (1 : 1) in non-polar solvents :**n*-Hexadecanol in decalin or cyclohexane :**

The variation of the dielectric constant ϵ' and the dielectric loss ϵ'' as a function of temperature on cooling and heating were measured for the different concentrations of *n*-hexadecanol in decalin and cyclohexane respectively. An example for these measurements is illustrated graphically in Figure 5 for *n*-hexadecanol in cyclohexane. On cooling, two freezing temperatures are detected indicating the presence of the gel phase in the temperature range between them. By dilution, this gel region is found to decrease till it vanishes at a certain concentration depending on the solvent used [9]. This could be attributed to the decrease in the concentration of dipoles N as discussed in the case of pure *n*-hexadecanol and the mixture of *n*-hexadecanol with *n*-octanol (1 : 1). It is also found that as the gel phase vanishes, the values of ϵ'' are very small to be measured. Variations with temperature of ϵ' and σ for very dilute solutions are very small. This implied the doubling of the scale just to show that for the most diluted solution there is only one freezing point. The curves of cooling and heating give rise to a picture of a hysteresis loop.

Mixture of *n*-hexadecanol and *n*-octanol (1 : 1) in decalin or cyclohexane :

The variation of the dielectric constant ϵ' as a function of temperature on cooling and heating was measured for the mixture of *n*-hexadecanol with *n*-octanol (1 : 1) in decalin and cyclohexane respectively. As mentioned before, no gel phase is expected to appear during

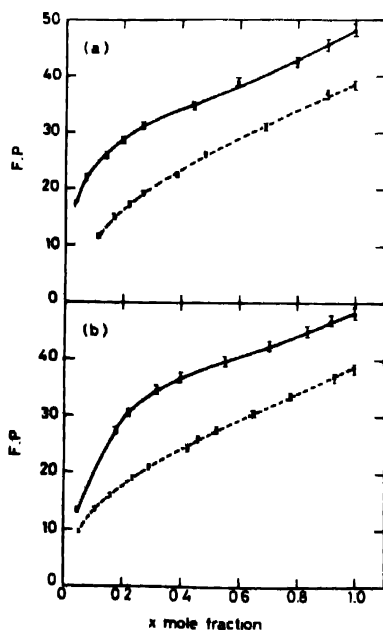


Figure 6. The freezing point (F.P.) versus the concentration x in mole fraction of *n*-hexadecanol and mixture of *n*-hexadecanol and *n*-octanol (1 : 1) in (a) decalin and (b) cyclohexane.

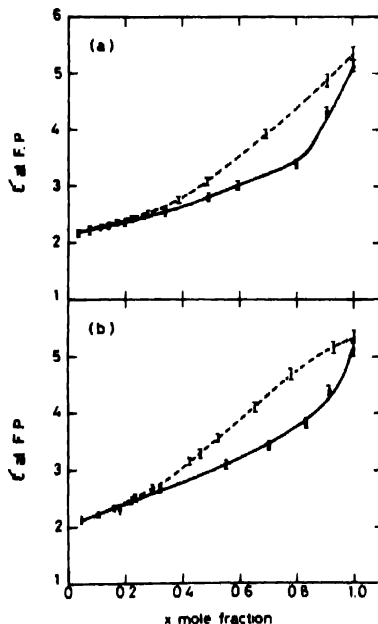


Figure 7. The dielectric constant at the freezing point (ϵ' at F.P.) versus concentration x in mole fraction of *n*-hexadecanol and mixture of *n*-hexadecanol and *n*-octanol (1 : 1) in (a) decalin and (b) cyclohexane.

solidification. Either on cooling or on heating, the behaviour is similar to that of the mixture of n-hexadecanol with n-octanol (1 : 1). The dilute solutions are also plotted on larger scale.

The difference between the value of ϵ' at the freezing point and its value at the threshold of the stable solid phase is known [30] as the dip. The value of the dip decreases as well with dilution.

Now, the evidences point towards the feasibility of studying the variation with concentration of the freezing point (F.P.), ϵ' at the freezing point as well as the dip of the investigated alcohols. The freezing point (F.P.) as well as the dielectric constant ϵ' at freezing point are plotted graphically *versus* the concentration x (in mole fraction) in Figures 6 and 7 respectively. These relations are represented by smooth curves.

The relation between the dip and the concentration x is plotted graphically in Figure 8 for n-hexadecanol and its mixture with n-octanol (1 : 1) in decalin and cyclohexane respectively. It is clear that this relation is represented by a smooth curve. The sharp increase

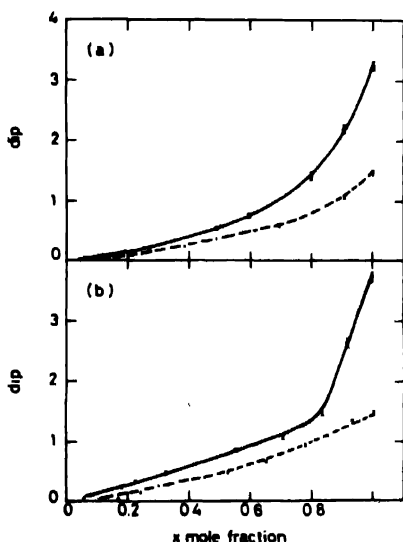


Figure 8. The dip *versus* concentration x in mole fraction on — n-hexadecanol and ... mixture of n-hexadecanol and n-octanol (1 : 1) in (a) decalin and (b) cyclohexane.

noticed in the case of n-hexadecanol in decalin or cyclohexane at concentrations more than 0.80 mole fraction could be attributed to the presence of the gel phase in these solutions.

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